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A DISSERTATION

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UNIVERSITY OF MICHIGAN

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Harry Freund
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Fractional Separation of Hafnium and Zirconium by Means of Triethylphosphate

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This study is an extension of previous work on separations in which the precipitating ion was not added as such, but formed slowly by hydrolysis in solution. The principles set forth in the original work on the slow formation of hydroxyl ion were confirmed. When the solution is homogeneous with respect to the precipitating ions, the precipitation of a normally gelatinous product may be improved to yield a dense, granular easily filterable precipitate, and a great improvement in the efficiency of separation of difficultly separable elements can be attained. Hafnium was separated from zirconium by fractional precipitation of the ethylphosphates obtained by hydrolysis of triethylphosphate in a boiling solution of 6 *N* sulfuric acid. Data from this separation were used to develop an optimum fractionation procedure, resulting in efficient separation of hafnium from a mixture containing a relatively low percentage of hafnium.

WHEN a precipitation reaction is used for the separation of ions, the formation of a gelatinous precipitate is a serious problem. The slimy nature of the product makes filtration difficult and inefficient washing leaves adsorbed and occluded impurities. If the precipitating ion is not added as such but is formed slowly and homogeneously throughout the body of the reaction mixture, and other conditions are fulfilled, a dense and granular precipitate is formed. This precipitate is easily filtered and washed and carries down few impurities, thus affording a simple means of solving the problem. Willard and his co-workers (3-6) successfully carried out the separation of hydroxides and basic salts from many ions by a gradual and uniform increase in pH resulting from the hydrolysis of urea.

This paper extends the work to the formation of ions other than hydroxyl, and the hydrolysis of triethylphosphate is employed successfully in the fractional separation of hafnium and

zirconium. Triethylphosphate is completely miscible with sulfuric acid solutions of zirconium and hafnium. When such a mixture is boiled, the ester is hydrolyzed in a stepwise manner and a precipitate of zirconyl or hafnium ethyl acid phosphate is produced. By using only sufficient ester to precipitate a fraction of the combined hafnium plus zirconium, the hafnium concentrates in the precipitate.

A systematic approach to the separation of zirconium and hafnium by direct fractional precipitation with phosphoric acid was developed by Larsen, Fernelius, and Quill (1), in whose paper the references to the literature of the phosphate method are given. The gelatinous nature of the precipitate was overcome by rigid control of the many factors influencing the precipitation reaction. In addition, a method of opening the ore with concentrated sulfuric acid and the solution of the phosphate precipitate were described and are used extensively in the present investigation.

STARTING MATERIAL

The source of the hafnium and zirconium salts was the mineral cyrtolite, an altered zircon containing about 5% hafnia by weight. The ore was crushed, ground to pass 100-mesh, and digested with concentrated sulfuric acid (1, 2). The resulting sulfate solution was then used directly for fractional precipitations or purified by precipitation of the hafnium and zirconium by means of excess triethylphosphate.

METHOD OF ANALYSIS

Two analyses were usually required, one for the combined hafnia and zirconia and the other for the hafnia present in the combined oxides. Whenever possible the determination of combined oxides was run first, the oxides were returned to solution by fusing with potassium bisulfate, and the resulting solution was used for the hafnium determination.

As no simple chemical process is available that will distinguish between hafnium and zirconium, it is necessary to have recourse to some indirect method. One of the most feasible is the conversion of a mixture of two well-defined hafnium and zirconium compounds into two other compounds.

Schumb and Pittman (2) published a method of determining hafnium in a mixture of hafnium and zirconium oxychlorides by conversion to the normal selenites followed by ignition to the oxides. Three changes were essential before the method could be applied to the mixtures in this investigation. (1) It was necessary to convert the sulfuric acid solutions of hafnium and zirconium into the corresponding hydrochloric acid solutions. This was accomplished by a double precipitation with ammonia followed by solution in 10 ml. of 1 to 1 hydrochloric acid. (2) It was necessary to destroy the wood sugars resulting from the hydrolysis of the cellulose (filter paper), by boiling the hydrochloric acid solutions with hydrogen peroxide. Following solution in 1 to 1 hydrochloric acid, the solution was boiled with 5 ml. of 30% hydrogen peroxide, and then diluted to 200 ml. for precipitation of the selenites with 50 ml. of 20% selenious acid. (3) It was necessary to remove the silica from the ignited oxides in the combined oxides determination. This was accomplished by evaporating cautiously 10 drops of concentrated sulfuric acid and 0.5 to 1 ml. of hydrofluoric acid from the oxides. The mixed

sulfates were then carefully ignited to the oxides, the final ignition being made at 950° C.

NATURE OF PRODUCT SEPARATED BY HYDROLYSIS OF TRIETHYLPHOSPHATE IN PRESENCE OF ZIRCONIUM

If the hydrolysis of triethylphosphate went to completion, zirconyl phosphate, $\text{ZrO}[\text{H}_2(\text{PO}_4)_2]$, would be precipitated. However, the stepwise hydrolysis of the ester results in the precipitation of zirconium ethyl phosphate.

A carefully purified sample was analyzed to obtain the loss on ignition and zirconium and phosphorus contents. On the basis of these results a suggested formula is $\text{ZrO}[\text{H}(\text{C}_2\text{H}_5)(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$. A comparison of the chemical analysis and calculated analysis is made in Table I.

Near the completion of this investigation trimethylphosphate became available and because of its increased rate of hydrolysis over that of triethylphosphate, some experiments were run to compare the two esters. The results indicated that the time required for the same degree of precipitation of zirconium by trimethylphosphate was about one third that required by the triethyl compound. This means a tremendous saving in time, since the usual fractionation procedure to produce relatively pure hafnium compounds with triethylphosphate requires five to six

Table I. Results in Analysis of Zirconium Compound Precipitated by Hydrolysis of Triethylphosphate

	Calculated	Experimental
Mole ratio P/Zr	2.00	2.00
% Zr	23.20	23.12 ± 0.06
% P	15.76	15.76 ± 0.03
% loss on ignition	32.55	32.6 ± 0.1
Molecular weight	393.2	393 ± 1

Table II. Degree of Fractionation in Sulfuric, Nitric, and Hydrochloric Acid Solutions

Type Solution	Mole Fraction	
	$\text{HfO}_2 + \text{ZrO}_2$ removed	HfO_2 removed
6 N sulfuric acid	0.333	0.623
6 N nitric acid	0.333	0.516
6 N hydrochloric acid	0.333	0.513

Table III. Effect of Free Acid on Fractionation of Hafnium

Normality of Sulfuric Acid	Initial Weight % HfO_2	Mole Fraction $\text{HfO}_2 + \text{ZrO}_2$ Removed	Final Weight % HfO_2
6	20.3	0.519	32.9
8	20.3	0.540	29.6
10	20.3	0.525	30.9
12	20.3	0.553	30.9
14	20.3	0.567	30.2

steps at 20 hours per step for the reaction time alone. Also, it is reasonable to expect that the product separated would be analogous to the zirconium ethyl phosphate and therefore would show about the same fractionation characteristics.

EFFECT OF ANION ON FRACTIONATION OF HAFNIUM

The usual explanation of the operation of a fractional precipitation method is based upon the slight difference in the solubility of the products. The ratio of the molecular solubilities of hafnium and zirconium phosphates in 6 *N* hydrochloric acid is only 1 to 4. Zirconium generally preponderates in the usual mixture of zirconium and hafnium, and the repressing effect of the high zirconium concentration should overbalance the slight differences in solubility. The fact that it does not suggests that relative stabilities of anionic complexes may be involved. If this is so, the fractionation should depend upon the anion present in the solution. To check this, the same fraction of the combined oxides was precipitated with triethylphosphate from 6 *N* solutions of sulfuric, nitric, and hydrochloric acids. The results, tabulated in Table II, indicate that the best results are obtained in a sulfuric acid solution.

EFFECT OF FREE ACID CONCENTRATION ON FRACTIONATION OF HAFNIUM

The effect of the free acid concentration was determined by precipitating approximately the same fraction of the combined oxides from solutions of varying sulfuric acid concentration. As shown in Table III, no noticeable improvement in the fractionation takes place as the acid concentration is varied.

6 *N* sulfuric acid was selected as the most desirable reaction medium, primarily for the dense, granular precipitate produced and also because the solutions were the least corrosive.

DEVELOPMENT OF AN OPTIMUM FRACTIONATION PROCEDURE

The development of an optimum fractionation procedure depends upon the application of a suitable criterion for determining the fraction of the total hafnia plus zirconia that should be precipitated at a given step. The highest concentration of hafnia in the product and the greatest recovery of hafnia are the two most important factors to be considered. Unfortunately they are dependent upon one another. If a relatively small amount of the total hafnium plus zirconium is precipitated, the hafnium content of the precipitated phase will be considerably higher than if a larger amount of the combined oxides had been separated. Thus as the yield of hafnia recovered in the precipitated phase is increased, the hafnium concentration is decreased.

At this point a clarification of the term "instantaneous composition" is required. The chemical analysis indicates the average composition over a given interval. If this interval were continually shortened, then at the limit the composition would represent an instantaneous value. Physically it would correspond to the composition of the product separating at a given instant, if all of the previously separated product could be removed.

From the above discussion it is apparent that the instantaneous composition of the separating phase will vary from high values of per cent hafnia to low values as the fractionation progresses. Therefore, the fractionation should be stopped at the point where the instantaneous composition of the separating product is equal

to the initial composition of the starting material. To carry the fractionation beyond this point would simply mean that the product was being diluted with a mixture less rich in hafnium than the starting material. Although there is no convenient way to determine experimentally the relation between the instantaneous composition and the fraction of the combined oxides precipitated, it can be deduced by graphical means from other data more easily measured. The first step is a comparison of

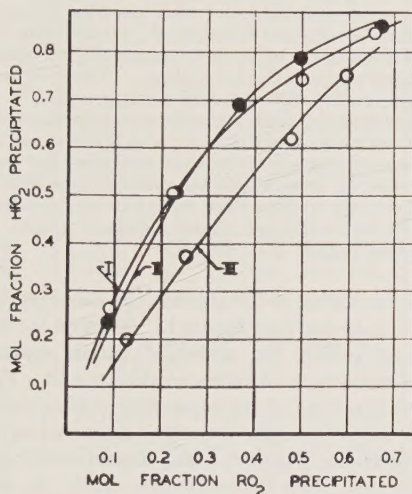


Figure 1. Comparison of Hafnia and Total Oxides Precipitated

Mole Fraction HfO_2 in Starting Material
 I. 0.0753
 II. 0.179
 III. 0.504

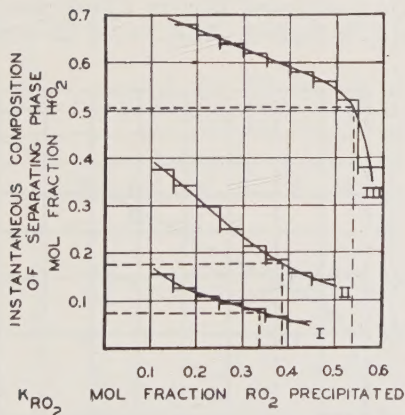


Figure 2. Relationship of Instantaneous Composition and Mole Fraction of Combined Oxides Precipitated

Initial Mole Fraction HfO_2	Optimum Cutoff K_{RO_2}
I. 0.0753	0.34
II. 0.179	0.39
III. 0.504	0.54

the fraction of the hafnia precipitated with the fraction of the combined oxides precipitated for initial mixtures containing varying amounts of hafnia, somewhat analogous to the treatment of Larsen *et al.* (1).

The experimental work consisted in carrying out a series of single precipitations on starting solutions having the same hafnia content, in which 10 to 70 mole % of the total oxides were precipitated as the ethylphosphates. Sufficient triethylphosphate (375 ml. of ester per mole of oxides) was added to solutions of 6 *N* sulfuric acid, containing 0.1 mole per liter of combined oxides, to precipitate the desired fraction of the oxides as the ethylphosphates. A mole ratio of ester to oxides slightly greater than 2 to 1 was required because of side reactions. The mixtures were boiled for 20 hours, cooled, filtered, and washed with 2% sulfuric acid. Sodium hydroxide-sodium peroxide mixtures were used to decompose the phosphate precipitate (1), and make it soluble in sulfuric acid. The resulting solutions were analyzed for both combined oxides and hafnia, from which the desired data were easily calculated. These experiments were repeated for solutions whose combined oxides had different initial hafnia contents. These data are plotted in Figure 1.

For selected values of the abscissa the corresponding ordinates are read from the curves of Figure 1. Then on the basis of 1 mole of combined oxides, the moles of hafnia separated and the increments in the moles of hafnia are determined. From these the average compositions of the separating phases corresponding to increments in the precipitation of the combined oxides are calculated and plotted in Figure 2. The instantaneous curve is drawn so that the area under the rectangles equals the area under the curve. The intersection of the instantaneous curve with the ordinate representing the initial composition gives the optimum cutoff in the fractionation. Obviously, if the curve relating the optimum cutoff and the initial composition were plotted, it would have to pass through the points 0,0 and 1,1. These data are made of more general value by putting them on a semilog plot as shown in Figure 3. Thus, for any given initial composi-

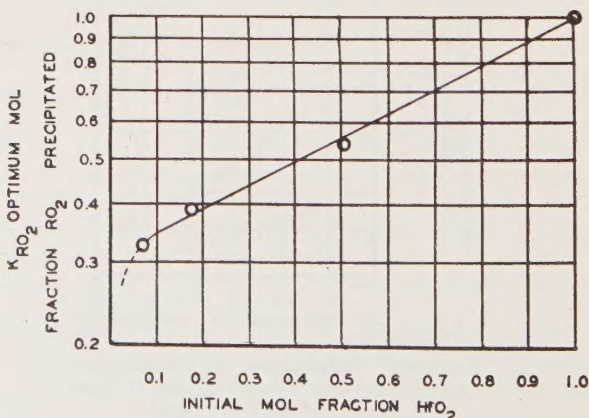


Figure 3. Comparison of Optimum Mole Fraction of Combined Oxides Precipitated and Composition of Starting Material

Table IV. Fractionation Series Using Optimum Procedure

Fractionation step	Experimental					Over-all efficiency		Composition mole fraction HfO ₂		Predicted Composition Mole fraction HfO ₂ from Fig. 4	Experimental Mole Fraction RO ₂ Precipitated	Desired Mole Fraction RO ₂ Precipitated from Fig. 3
	Weight of RO ₂ Grams	HfO ₂ Weight %	Solution volume Ml.	HfO ₂ Mole	Mole fraction HfO ₂ precipitated	HfO ₂ precipitated	ZrO ₂ Moles	RO ₂ Moles	Composition mole fraction HfO ₂			
1	Initial	215	16.0	0.163	0.664	0.664	1.464	1.627	0.100			
	Final	75.3	30.3	0.1081	0.664	0.664	0.425	0.531	0.203	0.19	0.328	0.34
2	Initial	74.1	30.3	0.1063	0.712	0.472	0.418	0.5243	0.203			
	Final	29.8	53.6	0.0757	0.712	0.472	0.1120	0.1877	0.403	0.35	0.358	0.38
3	Initial	28.9	53.6	0.0735	0.738	0.348	0.1089	0.1824	0.403			
	Final	15.1	75.8	0.0543	0.738	0.348	0.0296	0.0839	0.647	0.57	0.460	0.49
4	Initial	14.0	75.8	0.0503	0.878	0.306	0.0275	0.0778	0.647			
	Final	11.65	80.0	0.0442	0.878	0.306	0.0189	0.0631	0.700	0.75	0.812	0.66
5	Initial	10.48	80.0	0.0397	0.779	0.238	0.0170	0.0567	0.700			
	Final	7.16	91.1	0.0309	0.779	0.238	0.0052	0.0361	0.853	0.80	0.637	0.71

tion of combined oxides, the optimum extent of precipitation is determined from the curve. Again, considering 1 mole of combined oxides as a basis, and using the curves of Figures 1 and 3, the plot of Figure 4 relating the composition at steps $N + 1$ and N may be obtained. If the experimental data were very accurate and if rigid control could be maintained over the fractionation procedure, this curve would assist greatly in planning the entire fractionation series.

Using a 45° reference line, a series of steps in the fractionation process could be plotted. Unfortunately, the very small error per step adds to a very considerable cumulative error which greatly lessens its value with the data at present available.

APPLICATION OF OPTIMUM FRACTIONATION PROCEDURE TO FRACTIONATION SERIES

The procedure for using the fractionation curves consists in determining first the initial moles of combined oxides and the hafnia content of these oxides. Then using Figure 3 the desired

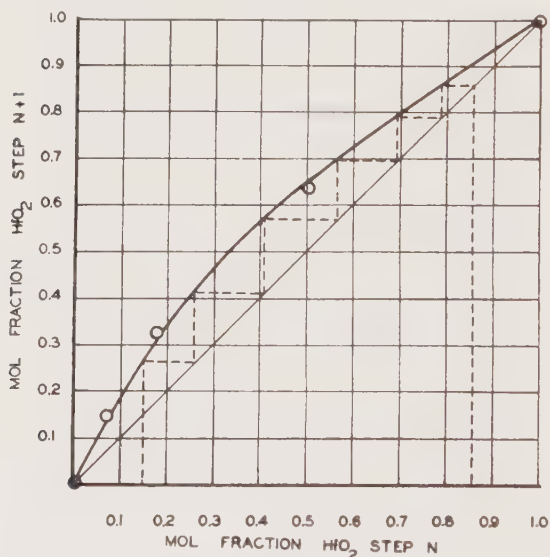


Figure 4. Comparison of Composition at Step $N + 1$ and at Step N

mole fraction of the combined oxides to be precipitated is selected and sufficient triethylphosphate is added to carry out the precipitation. The ethylphosphates are decomposed with a caustic peroxide mixture, and the acid-soluble product is dissolved in 6 N sulfuric acid and analyzed.

From the new analysis the next fractionation step may be planned as before. Figure 4 may be used to predict the composition one or two steps in advance. The data for an entire series are tabulated in Table IV. In this series 215 grams of combined oxides containing 16.0 weight % hafnia were enriched

to 7.16 grams of combined oxides containing 91.1 weight % hafnia in five steps. This represents an over-all efficiency in the recovery of hafnia of 23.8%.

LITERATURE CITED

- (1) Larsen, E. M., Fernelius, W. C., and Quill, L. L., *IND. ENG. CHEM., ANAL. ED.*, 15, 512-15 (1943).
- (2) Schumb, W. C., and Pittman, F. K., *Ibid.*, 14, 512-15 (1942).
- (3) Sheldon, J., doctoral thesis, "Study of Ferric Hydroxide Precipitated by Urea and Its Use in Quantitative Separations", University of Michigan, 1940.
- (4) Willard, H. H., and Fogg, H. C., *J. Am. Chem. Soc.*, 59, 1197 (1937).
- (5) Willard, H. H., and Tang, N. K., *IND. ENG. CHEM., ANAL. ED.*, 9, 357 (1937).
- (6) Willard, H. H., and Tang, N. K., *J. Am. Chem. Soc.*, 59, 1190 (1937).

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